Pergamon

Scripta Materialia, Vol. 39, No. 8, pp. 1157–1162, 1998
Elsevier Science Ltd

1359-6462/98 $19.00 + .00

PII S1359-6462(98)00280-2

THE PHASE EQUILIBRIUM CALCULATION OF SOLID SOLUTION WITH MAGNETIC TRANSITION BY CLUSTER VARIATION METHOD

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(Received December 29, 1997)
(Accepted in revised form June 29, 1998)

Introduction

The cluster variation method (CVM), proposed by R. Kikuchi in 1951 [1], is a statistical mechanics method to calculate the mixing entropy of solid solution. The CVM with the nature iteration method (NIM) can effectively calculate the phase equilibria between the same structure phases [2]. In recent years, the CVM has been developed further and applied in phase equilibrium calculations [3–4]. However, so far, it is still not reported that the CVM together with NIM is applied to calculate the phase equilibria between different structural phases with magnetic transition. This may be because that it is very difficult to construct the magnetic transition by the first principle, and the NIM can not directly be used to calculate these phase equilibria. In this paper, the free energy of solid solution with magnetic transition is investigated using the CVM combining with T. Nishizawa magnetic transition model [5]. The geometrical analysis of grand potential of solid solution with magnetic transition is carried out. A method of calculating phase equilibrium between different structural phases with magnetic transition is presented. This method is applied to the α/γ phase equilibria in the binary iron systems, the calculated phase diagrams approximate the experimental diagrams.

Model of Energy

The molar ferromagnetic free energy F_m^m equals the sum of molar paramagnetic free energy F_m^p and magnetic transition free energy ΔF_m. The F_m^p is described by the pair approximation of CVM as

$$F_m^p = \omega N_0\left(\sum_i \epsilon_{ii}x_i + \sum_i\sum_{j\neq i}\Delta\epsilon_{ij}y_{ij}\right) - TR\left[(2\omega-1)\sum_i x_i\ln x_i - \omega\sum_i\sum_j y_{ij}\ln y_{ij}\right]$$
$$= N_0\omega\sum_i \epsilon_{ii}x_i + \omega N_0\sum_I\sum_{j\neq i}\Delta\epsilon_{ij}y_{ij} - TS_m^p = \sum_i {}^0F_i x_i + \Delta U_m^p - TS_m^p. \quad (1)$$

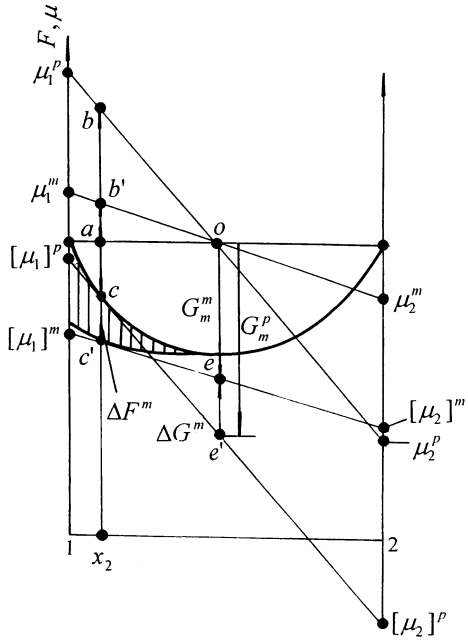

Figure 1. The expression of the grand potential in molar free energy diagram.

where S_m^p and ΔU_m^p are the molar paramagnetic mixing entropy and the paramagnetic mixing internal energy, respectively; N_0 is Avogadro number, R is gas constant; 2ω is the coordination number; ϵ_{ij} is the interaction energy between atom i and j, $\Delta\epsilon_{ij} = \epsilon_{ij} - (\epsilon_{ii} + \epsilon_{jj})/2$; y_{ij} is the probability of i-j atom pair, x_i is the molar fraction of component i. ${}^0F_i$ represents the free energy of pure component i.

On the other hand, the magnetic transition free energy is given by T.Nishizawa model as

$$\Delta F^m = (1 - \sum m_i x_i) \frac{T_c}{{}^0T_c} [\Delta\, {}^0F_{Fe}(T^*)]^m, \tag{2}$$

where m_i is magnetic coefficient. $m_i = 1$ for all nonmagnetic alloying elements, $m_i = 0$ for Co and Ni. ${}^0T_c$ and T_c are the curie temperature of pure iron and its solution. $[\Delta {}^0F_{Fe}(T^*)]^m$ is the ferromagnetic free energy of pure iron at the temperature $T^* = {}^0T_c/T_c$.

The molar paramagnetic grand potential is expressed by pair approximation of CVM as

$$G_m^p = \sum_i {}^0F_i x_i + \Delta U_m^p - TS_m^p - \sum_i \mu_i^p x_i, \tag{3}$$

where μ_i^p is paramagnetic effective chemical potential. In equilibrium condition $\partial G_m^p/\partial y_{ij} = 0$,

$$y_{ij} = (x_i x_j)^{\frac{2\omega-1}{2\omega}} \exp\left(-\frac{{}^0F_i + \Delta\epsilon_{ij}}{RT} + \frac{\mu_i^p + \mu_j^p}{2\omega RT} + \frac{\lambda}{\omega RT} \right). \tag{4}$$

Geometrical Analysis of Grand Potential

Fig. 1 expresses the molar free energy diagram of solution with magnetic transition in a binary system. The shadow part is the magnetic transition free energy. The molar paramagnetic free energy F_m^p and

magnetic transition free energy ΔF^m at composition x_2 equal line $\overrightarrow{ac}$ and $\overrightarrow{cc'}$, respectively. The molar ferromagnetic free energy F_m^p is line $\overrightarrow{ac'}$. The paramagnetic chemical potential $[\mu_i]^p$ is obtained by making the tangent of paramagnetic free energy curve through point c. The paramagnetic effective chemical potential μ_i^p is obtained by making a paralleling line of $\overline{[\mu_1]^p[\mu_2]^p}$ through the middle point o. $\Sigma\, x_i\mu_i^p$ equals line $\overrightarrow{ab}$. The paramagnetic grand potential is

$$G_m^p = F_m^p - \sum_{i=1}^{n} x_i\mu_i^p = \overrightarrow{ac} - \overrightarrow{ab} = \overrightarrow{ac} + \overrightarrow{ba} = \overrightarrow{bc} = \overrightarrow{oe'} = \frac{[\mu_1]^p + [\mu_2]^p}{2}. \tag{5}$$

Similarly, the ferromagnetic chemical potential $[\mu_i]^m$, as well as the ferromagnetic effective chemical potential μ_i^m can be obtained. Line $\bar{a}\dot{b}'$ equals $\Sigma\, x_i\mu_i^m$, and

$$[\mu_i]^m = [\mu_i]^p + \Delta[\mu_i]^m, \quad \mu_i^m = \mu_i^p + \Delta\mu_i^m, \quad \mu_1^m = \frac{[\mu_1]^m - [\mu_2]^m}{2} = -\mu_2^m \qquad i = 1, 2 \tag{6}$$

where $\Delta[\mu_i]^m$ and $\Delta\mu_i^m$ are the magnetic chemical potential and magnetic effective chemical potential. The ferromagnetic grand potential can be analyzed as

$$\begin{aligned} G_m^m &= F_m^m - \sum \mu_i^m x_i = \overrightarrow{ac'} - \overrightarrow{ab'} = (\overrightarrow{ac} + \overrightarrow{cc'}) - (\overrightarrow{ab} - \overrightarrow{b'b}) \\ &= F_m^p + \Delta F^m - \sum (\mu_i^p + \Delta\mu_i^m)x_i = (\overrightarrow{ac} - \overrightarrow{ab}) + (\overrightarrow{cc'} + \overrightarrow{b'b}) \\ &= F_m^p - \sum \mu_i^p x_i + \Delta F^m - \sum \Delta\mu_i^m x_i = G_m^p + \Delta G^m = \overrightarrow{oe'} + \overrightarrow{e'e} = \overrightarrow{oe} = .\frac{[\mu_1]^m + [\mu_2]^m}{2} \end{aligned} \tag{7}$$

Equations (6), (7) show that the ferromagnetic grand potential and ferromagnetic chemical potential can be separated into paramagnetic and magnetic terms.

Phase Equilibrium Calculation

For phase equilibrium calculation between nonmagnetic and magnetic phases, supposed that α phase is ferromagnetic, β phase is nonmagnetic, then the grand potential of α phase is

$$^{\alpha}G_m^m = {}^{\alpha}G_m^p + \Delta^{\alpha}G^m. \tag{8}$$

For α phase, the equilibrium composition can not be sought directly by the NIM due to the magnetic grand potential $\Delta^{\alpha}G^m$ resulting in asymmetry in eq. (8). The absolute convergence of NIM can not be assured. Therefore, we propose a phase equilibrium calculation method for the solid solution with magnetic transition by combining the NIM with T. Nishizawa magnetic transition free energy model. The calculation procedure of is as follows. A chemical potential $^{\alpha}\mu_2^p$ is chosen as the paramagnetic effective chemical potential of α phase. The equilibrium composition x_2 and the molar paramagnetic grand potential $^{\alpha}G_m^p$ corresponding to $^{\alpha}\mu_2^p$ can be obtained by the NIM. In binary system, it is assumed that component 1 is iron, component 2 is the other nonmagnetic or magnetic element. The magnetic grand potential $\Delta^{\alpha}G^m$ is derived from equation (2) as follows

$$\begin{aligned} \Delta^{\alpha}G^m &= \Delta^{\alpha}F^m - \Sigma\Delta^{\alpha}\mu_i^m x_i^{\alpha} = \frac{\Delta[^{\alpha}\mu_1]^m + \Delta[^{\alpha}\mu_2]^m}{2} \\ &= \frac{1}{2}\left\{(2 - m_2)\frac{T_c}{{}^0T_1^C}[\Delta\,{}^0F_1^{\alpha}(T^*)]^m + (1 - 2x_2)(1 - m_2x_2)\frac{dT_c}{dx_2}\frac{[\Delta^0H_1^{\alpha}(T^*)]^m}{{}^0T_1^C}\right\} \end{aligned} \tag{9}$$

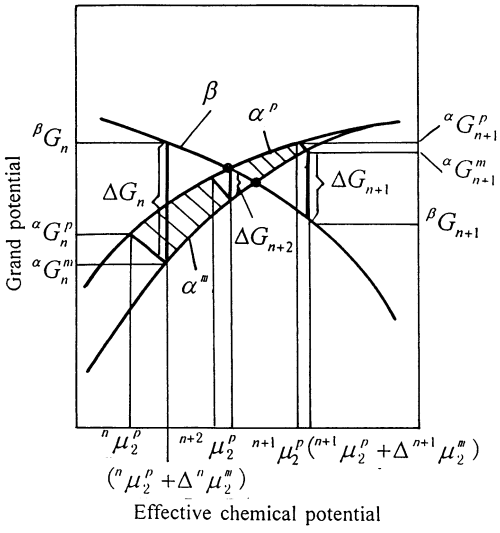

Figure 2. Schematic diagram of the DNIM used in the phase equilibrium calculation between ferromagnetic and nonmagnetic phases.

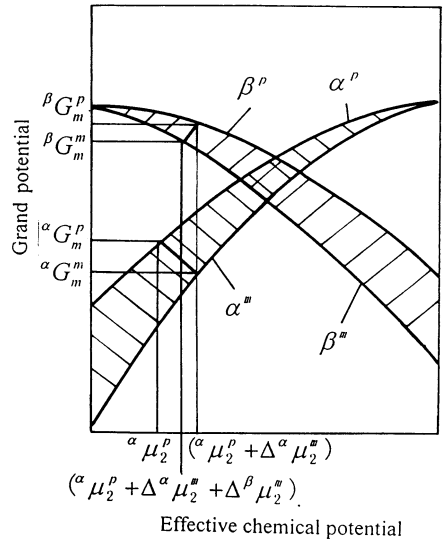

Figure 3. Schematic diagram of phase equilibrium calculation between two ferromagnetic phases.

where $[\Delta^0 H_1^{\alpha}\ (T^*)]^m$ is the ferromagnetic enthalpy of component 1 at the temperature T^*. Also, the ferromagnetic effective chemical potentials are obtained according to eq. (6). Based on equations (8), (9), the ferromagnetic grand potential ${}^{\alpha}G_m^m$ corresponding to composition x_2 can be calculated. Repeat the procedure above, the whole grand potential cures of α and β phases are obtained. The cross point between ${}^{\alpha}G_m^m$ and ${}^{\beta}G_m$ cures is sought by DNIM [6]. The whole calculation procedure is schematically shown in Fig. 2.

For the phase equilibrium calculation between two magnetic phases, supposed that α and β phases are all ferromagnetic phases. The paramagnetic grand potentials ${}^{\alpha}G_m^p$ and ${}^{\beta}G_m^p$ are calculated by the CVM with NIM. The magnetic grand potentials for the two phases are derived from the T.Nishizawa magnetic transition free energy model. The calculated procedure of grand potential is shown in Fig. 3, namely a chemical potential ${}^{\alpha}\mu_2^p$ is given as the paramagnetic effective chemical potential of α phase. The ferromagnetic grand potential of α phase corresponding to ${}^{\alpha}\mu_2^p = \Delta^{\alpha}\mu_2^m$ is calculated. Then ${}^{\alpha}\mu_2^p + \Delta^{\alpha}\mu_2^m$ is regarded as the paramagnetic effective chemical potential of β phase, the ferromagnetic grand potential of β phase corresponding to the ${}^{\alpha}\mu_2^p + \Delta^{\alpha}\mu_2^m + \Delta^{\beta}\mu_2^m$is calculated. The grand potential cures of α and β phases are obtained by repeating the procedure above. The equilibrium compositions are also calculated by the DNIM.

Result and Summary

In this paper, the α/γ phase equilibria in binary iron alloys, such as Fe-Mn, Fe-Al, Fe-Ti, and Fe-V systems, are calculated by pair approximation of CVM according to the above method. The interaction energies of Fe-M (Mn, Al, Ti, V) for α and γ phases are estimated from the literature [7–10]. The phase transition free energies for pure components are taken from references [11–15]. The calculated results and their comparison with the experimental results [16] are shown in Fig. 4. It shows that the calculated diagrams are in agree with the experimental diagrams.

The molar free energy of solution with magnetic transition can be well described by the cluster variation method combined with T.Nishizawa magnetic transition free energy model. A phase equi-

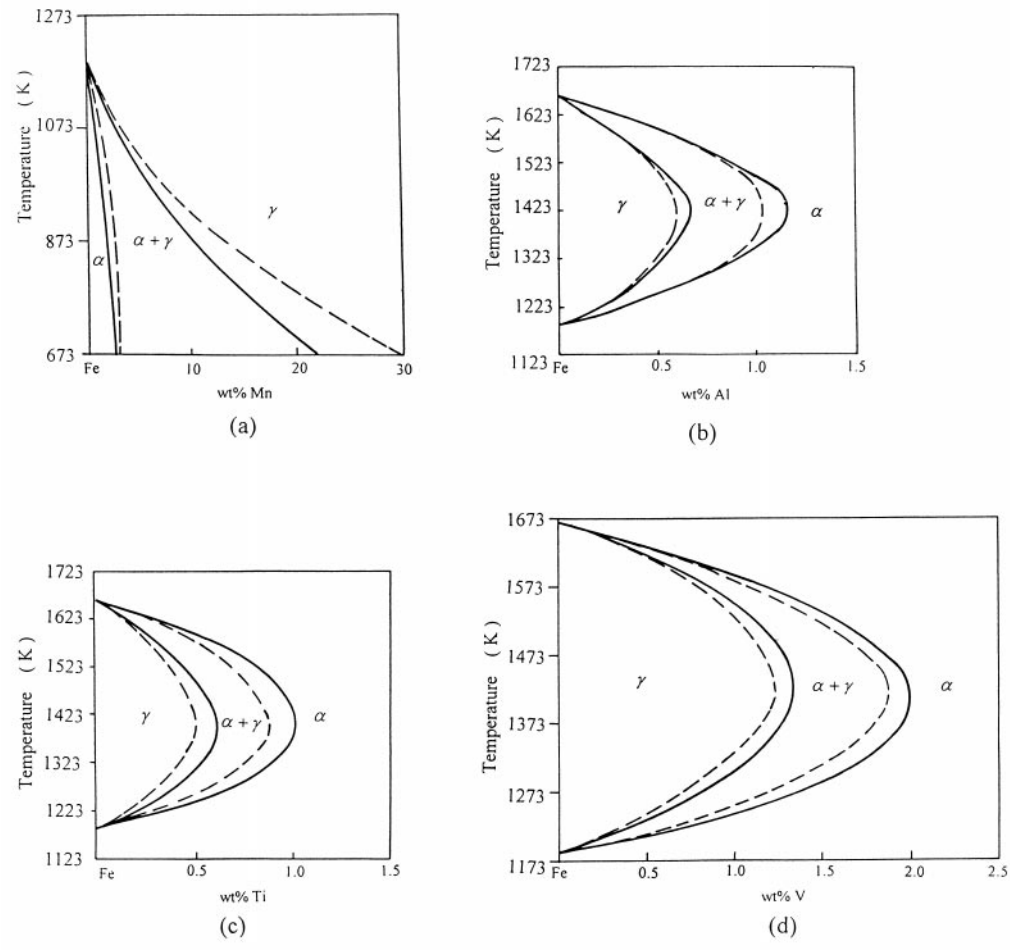

Figure 4. The calculated α/γ phase equilibria in (a) Fe-Mn, (b) Fe-Al, (c) Fe-Ti, and (d) Fe-V systems. The calculated α/γ phase boundaries using the CV-pair approximation of the CVM for the energy are given with solid lines. The experimental boundaries from ref. [16] are given with dashed lines.

librium calculation method for the solution with magnetic transition by the CVM is proposed. It is applied to the α/γ phase equilibria in the binary iron systems, the calculated phase diagrams approximate the experimental diagrams.

Acknowledgment

The work is supported by the National Natural Science Foundation of China (No. 59201007).

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